BLM LIBRARY
88069868

Report No. 22

UNITED STATES
DEPARTMENT OF THE INTERIOR

BUREAU OF MINES
HELIUM ACTIVITY
DIVISION OF RESEARCH

INTERNAL REPORT

AN EXPERIMENTAL STUDY OF THE PHASE RELATIONSHIPS OF EXELL GAS

BY

W. J. Boone, Jr.

Will E. DeVaney

John E. Miller

BRANCH Phase Equilibrium and Thermodynamics

PROJECT NO. 1540

DATE March 1960

HD
9660
.H43
M56
no.22

AMARILLO, TEXAS

#914811094

ID 88069868

HD
9660
.H43
M56
no.22

Report No. 22

DIVISION OF OPERATIONS RESEARCH

INTERNAL REPORT

AN EXPERIMENTAL STUDY OF THE PHASE RELATIONSHIPS OF EXELL GAS

By

W. J. Boone, Jr.
Will E. DeVaney
John E. Miller

Phase Equilibrium and Thermodynamics Branch

Project No. 1540

March 1960

BUREAU OF LAND MANAGEMENT LIBRARY
BLDG. 50,
DENVER FEDERAL CENTER
P.O. BOX 25047
DENVER, COLORADO 80225

AN EXPERIMENTAL STUDY OF THE PHASE RELATIONSHIPS OF EXELL GAS

INTRODUCTION

The Division of Operations Research has instituted a program to obtain phase equilibria data for helium-bearing natural gases which are of special interest to the Helium Activity. This plan encompasses the studies of gas processed for helium by our operating plants in addition to gases which give promise of becoming the source material for prospective plants. The actual study is performed on gas from which carbon dioxide, water, and hydrogen sulfide have been removed so that the experimental apparatus will not be plugged with solids which otherwise would form at the low temperatures encountered.

A number of phase studies have been made. The results of an experimental work (4) related to the gas supply for the Keyes Helium Plant, a new plant which recently went on stream, and a report (7) covering an experimental study of the Cliffside Gas, which has supplied the Amarillo Helium Plant for many years, have been submitted. A report (1) concerned with gas from the Rattlesnake Field, San Juan County, New Mexico, which gas provided the helium that was extracted for several years at the Navajo Helium Plant has been completed. Another report is in preparation for the Pan American Hogback Gas which likewise supplied this plant for a few years. Wells which provided both of these latter supplies are now inoperative. Reports (8, 9) relating to gas originating in the Hugoton Field, prominently mentioned as a possible source of helium-bearing gas for a new plant, have been prepared.

For the near future, two phase studies are contemplated. A study of the gas from the Pan American Navajo C-1 Well, which is currently supplying the Navajo Helium Plant, is proposed. A similar study of a Michigan-Wisconsin Pipeline Gas, a typical helium-bearing natural gas which originates in the Hugoton Field, is planned; the study of this gas is expected to be more comprehensive than that mentioned earlier (8) for a similar gas from this field.

The present report is a phase study related to the gas from which helium is extracted at the Exell Helium Plant. The gas originates in the Panhandle Field and is withdrawn from a pipeline of Colorado Interstate Gas Company for use by the plant. The Panhandle Field has supplied the Exell plant with gas since completion of the plant in 1943.

OBJECTIVES

There is a need for phase equilibria data pertaining to helium-bearing natural gases that are commercially important for helium extraction. There is a dearth of information in the literature on such systems. The current report that considers the Exell Gas, as well as the others already

submitted and those planned for the future, should provide data to meet some of this need.

The design of plant equipment and optimum operating conditions for helium-extraction processes hinge to considerable extent on phase equilibria data and other information derived therefrom. In order to simulate adequately the range of conditions feasible in plant operation, phase equilibria data were determined experimentally. Pressures of 100, 200, and 300 p.s.i.a. and temperatures in the range of -50 to -275° F., and pressures of 400 and 500 p.s.i.a. and temperatures in the range of -50 to -225° F. were chosen for study.

SUMMARY AND CONCLUSIONS

Two phase equilibrium apparatus, one of which is described in a previous report (2), were employed to obtain samples of equilibrium vapor and liquid phases. The results of mass spectrographic analysis of 120 samples for conditions in the temperature range of -50 to -275° F. and pressure range of 100 to 500 p.s.i.a. are reported. Results of an additional sample of each liquid phase (60 samples) analyzed by means of a helium analysis apparatus described essentially in (5) are also reported. The data presented in this report are representative of the gas stream immediately after removal of acidic gases and water by plant equipment at the Exell Helium Plant.

To simplify calculations, the gas system is considered for a portion of this study as one of four components: helium, nitrogen, methane, and ethane-plus. As noted in the report, nitrogen analyses that are reported include argon, oxygen, and hydrogen, which are present in very small concentrations. The sum of the concentrations of the latter three included in the nitrogen analysis for any sample does not exceed 0.3 mole percent in the extreme case and averages perhaps 0.1 percent.

Phase relationship data are presented in tabular form, Tables 2, 3, and following the scheme used in two earlier reports (7, 8) in graphical form, Figures 1-5. Curves for methane, nitrogen, and helium are shown in the vapor phase; similar data are shown for methane, nitrogen, and ethane-plus in the liquid phase. Data for helium in the liquid phase are not shown graphically because the values are too small to permit adequate representation on the scale employed in the graphs mentioned above. However, these data are presented in tabular form.

Additional phase relationship data are presented for ethane, propane, and butanes. These are shown in tabular form, Tables 4, 5. Supplementing the tabulations, graphical methods are employed to describe the data for ethane, Figure 6, and propane, Figure 7, in the equilibrium vapor and liquid phases, and for butanes (n-butane plus iso-butane) in the liquid phase, Figure 8.

A convenient and useful method of presenting a phase relationship

utilizes the ratio of the mole fraction of a given component in the vapor phase to its mole fraction in the liquid phase for an equilibrium condition at a certain temperature and pressure. Accordingly, these ratios (equilibrium vaporization coefficients) have been determined in most instances for methane, ethane-plus, nitrogen, and helium for each combination of pressure and temperature; these are presented in tabular form, Table 6. In addition, the coefficients are presented graphically for methane, Figure 9; the resulting smooth curves exhibit typical behavior for this component. Graphical presentation has not been included for the latter three components because of the scarcity of experimental points. Analytical limitations with respect to the small concentrations involved for certain conditions yield values which may have a large deviation from the true coefficients, and therefore result in erratic plots.

Solubility of helium is presented graphically as isobars by a plot of helium percent in liquid versus temperature, Figure 10. For the 400 and 500 p.s.i.a. isobars, the solubility of helium is low at -50° F. but, as temperatures are lowered, sharply rises to a maximum at cold temperatures (approximately -225° F.). For the 200 and 300 p.s.i.a. conditions, the solubility increases from a low value near -150° F. to a maximum value in the vicinity of -250° F. Owing to the scarcity of points, little can be concluded for the 100 p.s.i.a. condition beyond the fact that the solubility of helium in the liquid increases as colder temperatures are approached.

Liquefaction characteristics of natural gas are of special interest in helium production. Calculations of percent condensed are plotted versus temperature in isobaric form, Figure 11.

CONTENTS

Page

Composition of Exell Gas. 6

Experimental method. 7

Apparatus. 7

Procedures. 7

Presentation of data. 8

Vapor-liquid phase compositions. 8

Equilibrium vaporization coefficients. 26

Helium solubility. 26

Percent condensed. 26

Discussion of results. 31

Bibliography. 34

ILLUSTRATIONS

Fig.

1. Equilibrium phase relationships of Exell Gas, 100 p.s.i.a. 18
2. Equilibrium phase relationships of Exell Gas, 200 p.s.i.a. 19
3. Equilibrium phase relationships of Exell Gas, 300 p.s.i.a. 20
4. Equilibrium phase relationships of Exell Gas, 400 p.s.i.a. 21
5. Equilibrium phase relationships of Exell Gas, 500 p.s.i.a. 22
6. Equilibrium phase relationships of ethane in Exell Gas. 23
7. Equilibrium phase relationships of propane in Exell Gas. 24
8. Concentration of butanes in liquid phases, Exell Gas. 25
9. Equilibrium coefficients for methane, Exell Gas. 28
10. Solubility of helium in equilibrium liquid phases, Exell Gas. . . 29
11. Isobaric percent condensed data, Exell Gas. 30

TABLES

Page

1. Composition of Exell Gas (CO_2, H_2S, and H_2O-free) 6
2. Equilibrium phase relationships of Exell Gas as a four-component system, experimental data 9
3. Equilibrium phase relationships of Exell Gas as a four-component system, averaged experimental data 13
4. Equilibrium phase relationships of ethane, propane, and butanes in Exell Gas, experimental data 15
5. Equilibrium phase relationships of ethane, propane, and butanes in Exell Gas, averaged experimental data 17
6. Equilibrium vaporization coefficients of Exell Gas as a four-component system 27

COMPOSITION OF EXELL GAS

The gas which is processed for helium at the Exell Helium Plant originates in the western portion of the Panhandle Field and is removed from a gathering system of Colorado Interstate Gas Company. The carbon dioxide content of the inlet gas to the plant is about 0.8 percent, and a trace of hydrogen sulfide is also present. Plant equipment removes carbon dioxide, hydrogen sulfide, and water in advance of the helium separation process. It is this outlet stream (referred to as Exell Gas in this report) which provided the gas used in this investigation.

The Division of Operations Research received 22 cylinders containing Exell Gas in 3 groups of 10, 6, and 6 respectively. The first group was received early in October of 1958, the second group later in that month, and the third group in early November of 1958. The gas from each of the 22 cylinders was analyzed by means of the mass spectrometer. The analyses of the first group departed slightly from those of the second and third groups, but the differences were not considered significant. An average analysis of the gas content of the 22 cylinders is presented below in Table 1, both as a 14-component and four-component system. For the purpose of reporting the analysis on the basis of a four-component system, the following grouping is observed:

1) Methane
2) Hydrocarbons other than methane, consisting of ethane through hexanes-plus, considered as ethane-plus
3) Nitrogen, oxygen, argon, and hydrogen; designated as nitrogen
4) Helium

TABLE 1. - Composition of Exell Gas (CO_2, H_2S, and H_2O-free)

Component	As 14-Component System	As 4-Component System
Methane	73.2%	73.2%
Ethane	5.7	10.7
Propane	3.1	
n-Butane	.9	
i-Butane	.4	
n-Pentane	.1	
i-Pentane	.4	
Cyclopentane	.1	
Hexanes-plus	.1	
Nitrogen	15.0	15.1
Oxygen	[1]Trace	
Argon	.1	
Hydrogen	[1]Trace	
Helium	1.0	1.0

[1] Trace is less than 0.05 mole percent.

EXPERIMENTAL METHOD

Apparatus

Two Bureau of Mines Phase Equilibrium apparatus were used in this study. One of these has been described in a previous report (2). Essentially, the apparatus consists of a windowed equilibrium cell which can be maintained at any selected temperature in the range of room temperature to -320°F. and at any desired pressure from atmospheric to 800 p.s.i.g. in the case of one apparatus, up to 4000 p.s.i.g. in the second. Aside from pressure range, the two apparatus differ mainly in the method employed for temperature control. The apparatus designed for the higher pressure range utilizes a pneumatic system for temperature control and thermocouples within the cell itself for temperature measurement.

Procedure

Gas from the supply cylinder was admitted to the apparatus where it is passed through a scrubber containing potassium hydroxide to insure complete removal of water and carbon dioxide. The gas was regulated to the desired pressure and entered the windowed cell maintained at the chosen temperature. When desirable, a small flow of the vapor phase was allowed to flow through the cell to permit the accumulation of liquid phase.

The cell contents were stirred continuously in advance of sampling to promote rapid equilibrium. After equilibrium has been established, samples of both phases were withdrawn in quick succession for subsequent analysis by the mass spectrometer. An additional sample of each equilibrium liquid phase was taken for helium analysis by means of a special helium analytical apparatus described essentially in a previous publication (5). During sampling, a stirring device, the essential features of which have been described in a prior article (3), continuously mixed each phase while samples of vapor phase were withdrawn. For those conditions where the quantity of the liquid phase was small, stirring was not employed during sampling of this phase.

Temperature measurements were made with the use of a copper-constantan thermocouple. In the low-pressure apparatus, which was used for the greater part of this study, this thermocouple was in contact with the cell block and terminated about 1/8-inch from the equilibrium chamber and approximately midway the height of the cell. In the high-pressure apparatus the thermocouple junction is located inside the experimental chamber. The thermocouple output was measured with a portable precision potentiometer (Rubicon Company, Philadelphia, Pennsylvania). The temperature was controlled within ± 0.5° F. of the desired temperature for a period of 15-30 minutes prior to sampling.

The pressure on the contents of the cell at equilibrium conditions was controlled within approximately 2 p.s.i. of the desired pressure by means of a reducing regulator (Grove Model 94 Reducing Valve, Grove Regulator Company, Oakland, California).

PRESENTATION OF DATA

Vapor-Liquid Phase Compositions

Results of gas analysis of 180 samples of equilibrium vapor and liquid phases for 42 experimental conditions are presented in Table 2, with the Exell Gas reported as a four-component system. Sixty samples each of the respective vapor and liquid phases were analyzed with a mass spectrometer, and an additional sample of each liquid phase were analyzed for helium with a helium analysis apparatus. Table 3 was prepared with the aid of Table 2 to show averaged experimental data. The results of several samples which are noted as discarded in Table 2 are not averaged in Table 3.

Additional data from the 120 mass spectrometer analyses are presented to show the respective content of ethane, propane, and butanes in equilibrium phases of Exell Gas. These are given in Table 4, and, with the aid of this table, Table 5 was prepared to show the averaged experimental data. Again, results noted as discarded for several samples listed in Table 4 are not averaged in Table 5.

Equilibrium phase relationship data shown in Table 3 are plotted as isobars for 100, 200, 300, 400, and 500 p.s.i.a. in Figures 1 through 5, respectively. For each graph the concentrations of methane, nitrogen, and helium are plotted for the vapor phase, while the contents of ethane-plus, methane, and nitrogen are shown graphically for the liquid phase.

Table 5 is utilized to provide data for the following plots. Equilibrium phase relationships for ethane and propane are shown graphically as isobars in Figures 6 and 7, respectively. Concentrations of butanes (n-butane plus iso-butane) in the liquid phases are plotted as isobars in Figure 8.

The data for seven experimental runs for the 100 p.s.i.a. and -200° F. condition are shown in Table 2 and Table 4. These runs provided, in addition to the usual information determined in a phase study, a check of the overall precision of the method used in obtaining the phase equilibria data. The results of the mass spectrometer analysis of the sample obtained from the liquid phase for Run No. 2 were discarded because of the wide variance of the contents of nitrogen and ethane-plus from their respective averages for the seven runs. The mass spectrometer results for the liquid phase sample for Run No. 5 were likewise discarded because the contents of methane, ethane, propane, and ethane-plus varied appreciably from their respective averages for the seven runs. The helium contents in the vapor and liquid phases for these runs are respectively in excellent agreement. The results for the helium in the liquid phase are conditioned

TABLE 2. - Equilibrium phase relationships of Exell Gas as a four-component system, experimental data

Vapor phase													
Pressure, p.s.i.a.		100				200				300			
Component		Methane	Ethane-plus	Nitrogen	Helium	Methane	Ethane-plus	Nitrogen	Helium	Methane	Ethane-plus	Nitrogen	Helium
		%	%	%	%	%	%	%	%	%	%	%	%
Temperature, °F.	Run No.												
-50	1	74.5	9.4	15.2	0.9	75.2	8.3	15.5	1.0	75.7	7.6	15.7	1.0
	2									75.7	7.5	15.8	1.0
-100	1	76.4	6.7	15.8	1.0	77.4	5.2	16.3	1.0	77.9	4.4	16.7	1.1
	2									77.7	4.5	16.8	1.1
	3									77.7	4.5	16.7	1.1
-125	1	77.7	4.7	16.5	1.0	78.4	3.3	17.2	1.1	78.5	2.6	17.8	1.1
-150	1	79.0	3.0	17.0	1.1	79.1	1.7	18.2	1.1	77.9	1.1	19.7	1.3
-175	1	79.8	1.4	17.7	1.1	78.1	.5	20.1	1.2	63.8	.3	33.1	2.8
-200	1	78.1	.4	20.3	1.2	52.9	.4	42.9	3.9	42.4	.2	48.0	9.4
	2	77.7	.3	20.7	1.2	53.3	.2	42.5	4.0				
	3	77.5	.3	20.8	1.4								
	4	78.4	.3	20.0	1.3								
	5	78.2	.3	20.1	1.4								
	6	78.5	.3	20.0	1.2								
	7	78.5	.3	19.9	1.2								
-225	1	50.4	.1	45.7	3.8	29.7	.1	54.6	15.7	21.5	.1	43.5	34.8
-250	1	21.3	.1	62.7	15.9	14.0	.2	42.5	43.3	10.6	.1	30.3	59.0
-275	1	7.4	.0	43.8	48.8	3.7	.1	23.0	73.2	1/3.8	1/Tr.	1/18.5	1/77.7

% denotes mole percent.
Tr. is less than 0.05 mole percent.
1/ Data obtained at 298 p.s.i.a. instead of 300 p.s.i.a.

TABLE 2. - Equilibrium phase relationships of Exell Gas as a four-component system, experimental data (Con.)

Vapor phase									
Pressure		400				500			
Component		Methane	Ethane-plus	Nitrogen	Helium	Methane	Ethane-plus	Nitrogen	Helium
		%	%	%	%	%	%	%	%
Temperature, °F.	Run No.								
-50	1	75.7	7.4	15.9	1.0	76.3	6.7	16.0	1.0
	2	76.0	7.1	15.8	1.1				
-100	1	77.7	3.9	17.3	1.0	77.7	3.5	17.6	1.2
	2	78.0	3.9	17.1	1.1	77.5	3.7	17.7	1.1
-125	1	78.4	2.1	18.3	1.2	77.1	1.9	19.7	1.3
	2					76.4	2.0	20.2	1.4
-150	1	73.0	1.0	24.5	1.6	65.6	.9	30.6	2.9
	2					66.6	.8	29.8	2.9
-175	1	54.4	.4	39.2	6.0	46.9	.3	41.1	11.7
	2					46.6	.9	40.5	12.0
-200	1	33.3	.3	43.5	22.9	27.2	.6	36.7	35.5
	2					27.5	.2	37.5	34.8
-225	1	15.3	.1	34.5	50.1	13.5	.7	30.4	55.3
-250	1	[2]17.5	[2].6	[2]27.8	[2]54.1				
	2	6.8	Tr.	22.2	71.0				

% denotes mole percent.
Tr. is less than 0.05 mole percent.
[2] Apparently a poor sample (results discarded).

TABLE 2. - Equilibrium phase relationships of Exell Gas as a four-component system, experimental data (Con.)

Liquid phase													
Pressure, p.s.i.a.		100				200				300			
Component		Methane	Ethane-plus	Nitrogen	Helium	Methane	Ethane-plus	Nitrogen	Helium	Methane	Ethane-plus	Nitrogen	Helium
		%	%	%	%	%	%	%	%	%	%	%	%
Temperature, °F.	Run No.												
-50	1	7.4	91.5	1.1	0.001	13.9	84.7	1.4	0.002	17.8	81.1	1.2	0.008
	2									18.3	80.2	1.5	.009
-100	1	9.7	90.2	.2	.001	17.6	82.4	Tr.	.003	25.7	74.1	.2	2/ .021
	2									27.0	72.9	.1	.006
										25.7	73.4	.9	.009
-125	1	12.6	87.4	.1	.003	25.9	74.1	Tr.	.001	38.6	61.0	.4	.010
-150	1	19.9	78.7	1.4	.003	38.9	61.0	.1	.004	60.3	38.5	1.2	.005
-175	1	31.5	68.5	.1	.006	65.7	33.0	1.3	.004	82.3	17.6	.1	.006
-200	1	58.4	41.4	.2	.002	78.6	14.4	7.1	2/ .112	75.6	12.2	12.1	.090
	2	2/ 57.3	2/ 37.7	2/ 5.0	.002	76.6	17.1	6.2	.017				
	3	55.7	43.7	.6	.002								
	4	55.7	43.8	.5	.001								
	5	2/ 48.9	2/ 50.1	2/ 1.0	.001								
	6	56.8	42.3	.9	.002								
	7	56.8	40.8	2.2	003								
-225	1	79.9	15.5	4.6	.006	74.7	13.9	11.4	.029	75.3	10.3	14.3	.116
-250	1	76.4	11.7	11.9	.007	74.4	11.1	14.4	.070	74.0	11.0	14.9	.115
-275	1	74.1	11.7	14.1	.022	72.5	13.6	13.9	.054	1/ 74.2	1/ 10.4	1/ 15.2	1/ .101

% denotes mole percent.
Tr. is less than 0.05 mole percent.
1/ Data obtained at 298 p.s.i.a. instead of 300 p.s.i.a.
2/ Apparently a poor sample (results discarded).

TABLE 2. - Equilibrium phase relationships of Exell Gas as a four-component system, experimental data (Con.)

Liquid phase									
Pressure, p.s.i.a.		400				500			
Component		Methane	Ethane-plus	Nitrogen	Helium	Methane	Ethane-plus	Nitrogen	Helium
		%	%	%	%	%	%	%	%
Temperature, °F.	Run No.								
-50	1	24.8	73.9	1.3	0.006	30.7	67.5	1.8	0.007
	2	23.3	75.5	1.2	.003				
-100	1	37.2	62.2	.6	2/ .018	58.1	40.2	1.7	.017
	2	36.1	62.8	1.1	.008	56.3	41.9	1.7	.010
-125	1	51.1	47.3	1.5	.007	61.7	35.6	2.8	.020
	2					2/ 57.1	2/ 39.9	2/ 2.6	.024
-150	1	71.2	24.7	4.2	.014	72.5	20.6	6.9	.078
	2					2/ 62.5	2/ 34.0	2/ 3.5	.042
-175	1	74.7	15.3	10.0	.070	75.0	11.3	13.5	.203
	2					72.4	14.4	13.0	2/ .005
-200	1	74.6	10.9	14.3	.193	73.9	10.9	14.8	.361
	2					74.3	11.4	13.9	.343
-225	1	73.9	10.9	14.9	.238	73.5	10.6	15.5	.350
-250	1	73.3	12.5	14.0	.214				
	2	72.4	12.9	14.5	.168				

% denotes mole percent.
2/ Apparently a poor sample (results discarded).

TABLE 3. - Equilibrium phase relationships of Exell Gas as a four-component system, averaged experimental data

Pressure, p.s.i.a.		100				200				300			
Component		Methane	Ethane-plus	Nitrogen	Helium	Methane	Ethane-plus	Nitrogen	Helium	Methane	Ethane-plus	Nitrogen	Helium
		%	%	%	%	%	%	%	%	%	%	%	%
Temperature, °F.	Phase												
-50	Vapor	74.5	9.4	15.2	0.9	75.2	8.3	15.5	1.0	75.7	7.6	15.8	1.0
	Liquid	7.4	91.5	1.1	.001	13.9	84.7	1.4	.002	18.1	80.7	1.4	.009
-100	Vapor	76.4	6.7	15.8	1.0	77.4	5.2	16.3	1.0	77.8	4.5	16.7	1.1
	Liquid	9.7	90.2	.2	.001	17.6	82.4	Tr.	.003	26.1	73.5	.4	.008
-125	Vapor	77.7	4.7	16.5	1.0	78.4	3.3	17.2	1.1	78.5	2.6	17.8	1.1
	Liquid	12.6	87.4	.1	.003	25.9	74.1	Tr.	.001	38.6	61.0	.4	.010
-150	Vapor	79.0	3.0	17.0	1.1	79.1	1.7	18.2	1.1	77.9	1.1	19.7	1.3
	Liquid	19.9	78.7	1.4	.003	38.9	61.0	.1	.004	60.3	38.5	1.2	.005
-175	Vapor	79.8	1.4	17.7	1.1	78.1	.5	20.1	1.2	63.8	.3	33.1	2.8
	Liquid	31.5	68.5	.1	.006	65.7	33.0	1.3	.004	82.3	17.6	.1	.006
-200	Vapor	78.1	.3	20.3	1.3	53.1	.3	42.7	4.0	42.4	.2	48.0	9.4
	Liquid	56.7	42.4	.9	.002	77.6	15.8	6.7	.017	75.6	12.2	12.1	.090
-225	Vapor	50.4	.1	45.7	3.8	29.7	.1	54.6	15.7	21.5	.1	43.5	34.8
	Liquid	79.9	15.5	4.6	.006	74.7	13.9	11.4	.029	75.3	10.3	14.3	.116
-250	Vapor	21.3	.1	62.7	15.9	14.0	.2	42.5	43.3	10.6	.1	30.3	59.0
	Liquid	76.4	11.7	11.9	.007	74.4	11.1	14.4	.070	74.0	11.0	14.9	.115
-275	Vapor	7.4	.0	43.8	48.8	3.7	.1	23.0	73.2	1/ 3.8	1/ Tr.	1/ 18.5	1/ 77.7
	Liquid	74.1	11.7	14.1	.022	72.5	13.6	13.9	.054	1/ 74.2	1/ 10.4	1/ 15.2	1/ .101

% denotes mole percent.
Tr. is less than 0.05 mole percent.
1/ Data obtained at 298 p.s.i.a. instead of 300 p.s.i.a.

TABLE 3. - Equilibrium phase relationships of Exell Gas as a four-component system, averaged experimental data (Con.)

Pressure		400				500			
Component		Methane	Ethane-plus	Nitrogen	Helium	Methane	Ethane-plus	Nitrogen	Helium
		%	%	%	%	%	%	%	%
Temperature, °F.	Phase								
-50	Vapor	75.9	7.3	15.9	1.1	76.3	6.7	16.0	1.0
	Liquid	24.1	74.7	1.3	.005	30.7	67.5	1.8	.007
-100	Vapor	77.9	3.9	17.2	1.1	77.6	3.6	17.7	1.2
	Liquid	36.7	62.5	.9	.008	57.2	41.1	1.7	.014
-125	Vapor	78.4	2.1	18.3	1.2	76.8	2.0	20.0	1.4
	Liquid	51.1	47.3	1.5	.007	61.7	35.6	2.8	.022
-150	Vapor	73.0	1.0	24.5	1.6	66.1	.9	30.2	2.9
	Liquid	71.2	24.7	4.2	.014	72.5	20.6	6.9	.060
-175	Vapor	54.4	.4	39.2	6.0	46.8	.6	40.8	11.9
	Liquid	74.7	15.3	10.0	.070	73.7	12.9	13.3	.203
-200	Vapor	33.3	.3	43.5	22.9	27.4	.4	37.1	35.2
	Liquid	74.6	10.9	14.3	.193	74.1	11.2	14.4	.352
-225	Vapor	15.3	.1	34.5	50.1	13.5	.7	30.4	55.3
	Liquid	73.9	10.9	14.9	.238	73.5	10.6	15.5	.350
-250	Vapor	6.8	Tr.	22.2	71.0				
	Liquid	72.9	12.7	14.3	.191				

Tr. is less than 0.05 mole percent.

TABLE 4. - Equilibrium phase relationships of ethane, propane, and butanes in Exell Gas, experimental data

		Vapor phase														
Pressure, p.s.i.a.		100			200			300			400			500		
Component		Ethane	Propane	Butanes	Ethane	Propane	Butanes	Ethane	Propane	Butanes	Ethane	Propane	Butanes	Ethane	Propane	Butanes
		%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
Temperature, °F.	Run No.															
-50	1	5.5	2.8	0.9	5.4	2.3	0.6	5.2	2.0	0.4	5.4	1.8	0.2	4.8	1.6	0.2
	2							5.1	1.9	.3	5.1	1.8	.2			
-100	1	5.1	1.4	.1	4.3	.8	.1	3.7	.6	.1	3.4	.5	Tr.	3.0	.5	.0
	2							3.8	.6	.1	3.3	.5	Tr.	3.2	.5	.1
	3							3.8	.6	.1						
-125	1	4.1	.6	.0	3.0	.3	.0	2.4	.3	.0	1.9	.2	.0	1.7	.2	.0
	2													1.8	.2	.0
-150	1	2.8	.2	.0	1.6	.1	.0	1.1	.1	.0	.7	Tr.	.2	.7	.1	.1
	2													.7	.1	.0
-175	1	1.3	.1	.0	.5	Tr.	.0	.3	Tr.	.0	.3	.1	.0	.2	.1	.0
	2													.4	.2	.1
-200	1	.3	Tr.	.1	.1	Tr.	.1	.1	Tr.	.0	.1	Tr.	.1	.2	.2	.1
	2	.3	Tr.	.0	.2	Tr.	.0							.2	.1	.0
	3	.3	.0	.0												
	4	.3	Tr.	.0												
	5	.3	Tr.	.0												
	6	.3	Tr.	.0												
	7	.3	Tr.	.0												
-225	1	.1	.0	.0	.1	.0	.0	.1	Tr.	.0	Tr.	.1	.0	.1	Tr.	.2
-250	1	.0	Tr.	Tr.	.0	Tr.	Tr.	Tr.	Tr.	.1	1/.3	1/.1	1/.1			
	2										.0	Tr.	.0			
-275	1	.0	.0	.0	.1	Tr.	.0	2/.0	2/Tr.	2/.0						

Tr. is less than 0.05 mole percent.
1/ Apparently a poor sample (results discarded).
2/ Data obtained at 298 p.s.i.a. instead of 300 p.s.i.a.

TABLE 4. - Equilibrium phase relationships of ethane, propane, and butanes in Exell Gas, experimental data (Con.)

		Liquid phase														
Pressure, p.s.i.a.		100			200			300			400			500		
Component		Ethane	Propane	Butanes	Ethane	Propane	Butanes	Ethane	Propane	Butanes	Ethane	Propane	Butanes	Ethane	Propane	Butanes
		%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
Temperature, °F.	Run No.															
-50	1	7.8	24.3	37.1	12.0	29.1	29.8	15.1	30.3	24.6	15.7	26.5	20.6	16.8	25.0	17.5
	2							14.0	29.5	24.9	16.7	29.0	21.0			
-100	1	15.2	38.6	25.4	22.5	34.4	18.1	24.5	28.8	14.7	24.2	22.5	10.8	22.6	13.5	3.5
	2							24.3	27.9	14.0	23.0	22.1	11.8	22.9	14.5	3.9
	3							23.0	28.8	14.7						
-125	1	22.7	37.3	19.0	28.4	27.1	12.8	25.2	21.1	10.1	21.3	15.4	7.1	15.6	11.2	5.8
	2													[1] 19.6	[1] 13.3	[1] 5.0
-150	1	32.6	30.3	12.1	28.8	20.2	8.6	20.6	11.9	4.7	12.2	7.5	3.3	8.8	7.0	3.7
	2													[1] 17.9	[1] 11.3	[1] 3.9
-175	1	34.3	22.3	9.1	17.2	9.7	4.2	9.2	5.0	2.2	7.1	4.5	2.4	5.9	3.2	1.4
	2													6.4	4.0	2.3
-200	1	21.9	12.1	5.2	7.7	4.1	1.8	6.4	3.5	1.6	5.7	3.2	1.4	5.9	3.2	1.4
	2	[1] 19.3	[1] 11.2	[1] 5.1	8.1	4.8	2.6							6.2	3.4	1.4
	3	21.8	13.3	5.8												
	4	22.0	13.1	5.7												
	5	[1] 26.4	[1] 14.6	[1] 6.0												
	6	21.8	12.7	5.6												
	7	21.1	12.2	5.2												
-225	1	8.3	4.5	1.9	6.7	3.8	2.1	5.9	3.0	1.0	5.7	3.2	1.4	5.7	3.1	1.3
-250	1	6.3	3.3	1.4	5.9	3.2	1.4	5.7	3.2	1.4	6.2	3.5	1.7			
	2										6.1	4.2	2.1			
-275	1	5.9	3.3	1.5	6.0	3.4	2.0	[2] 5.5	[2] 3.0	[2] 1.3						

[1] Apparently a poor sample (results discarded).
[2] Data obtained at 298 p.s.i.a. instead of 300 p.s.i.a.

TABLE 5. - Equilibrium phase relationships of ethane, propane, and butanes in Exell Gas, averaged experimental data

Pressure, p.s.i.a.		100			200			300			400			500		
Component		Ethane	Propane	Butanes	Ethane	Propane	Butanes	Ethane	Propane	Butanes	Ethane	Propane	Butanes	Ethane	Propane	Butanes
		%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
Temperature, °F.	Phase															
-50	Vapor	5.5	2.8	0.9	5.4	2.3	0.6	5.2	2.0	0.4	5.3	1.8	0.2	4.8	1.6	0.2
	Liquid	7.8	24.3	37.1	12.0	29.8	29.8	14.6	29.9	24.8	16.2	27.8	20.8	16.8	25.0	17.5
-100	Vapor	5.1	1.4	.1	4.3	.8	.1	3.8	.6	.1	3.4	.5	Tr.	3.1	.5	.1
	Liquid	15.2	38.6	25.4	22.5	34.4	18.1	23.9	28.5	14.5	23.6	22.3	11.3	22.8	14.0	3.7
-125	Vapor	4.1	.6	.0	3.0	.3	.0	2.4	.3	.0	1.9	.2	.0	1.8	.2	.0
	Liquid	22.7	37.3	19.0	28.4	27.1	12.8	25.2	21.1	10.1	21.3	15.4	7.1	15.6	11.2	5.8
-150	Vapor	2.8	.2	.0	1.6	.1	.0	1.1	.1	.0	.7	Tr.	.2	.7	.1	.1
	Liquid	32.6	30.3	12.1	28.8	20.2	8.6	20.6	11.9	4.9	12.2	7.5	3.3	8.8	7.0	3.7
-175	Vapor	1.3	.1	.0	.5	Tr.	.0	.3	Tr.	.0	.3	.1	.0	.3	.2	.1
	Liquid	34.3	22.3	9.1	17.2	9.7	4.2	9.2	5.0	2.2	7.1	4.5	2.4	6.2	3.6	1.9
-200	Vapor	.3	Tr.	Tr.	.2	Tr.	.1	.1	Tr.	.0	.1	Tr.	.1	.2	.2	.1
	Liquid	21.7	12.7	5.5	7.9	4.5	2.2	6.4	3.5	1.6	5.7	3.2	1.4	6.1	3.3	1.4
-225	Vapor	.1	.0	.0	.1	.0	.0	.1	Tr.	.0	Tr.	.1	.0	.1	Tr.	.2
	Liquid	8.3	4.5	1.9	6.7	3.8	2.1	5.9	3.0	1.0	5.7	3.2	1.4	5.7	3.1	1.3
-250	Vapor	.0	Tr.	Tr.	.0	Tr.	Tr.	Tr.	Tr.	.1	.0	Tr.	.0			
	Liquid	6.3	3.3	1.4	5.9	3.2	1.4	5.7	3.2	1.4	6.2	3.9	1.9			
-275	Vapor	.0	.0	.0	.1	Tr.	.0	1/ .0	1/ Tr.	1/ .0						
	Liquid	5.9	3.3	1.5	6.0	3.4	2.0	1/ 5.5	1/ 3.0	1/ 1.3						

Tr. is less than 0.05 mole percent.

1/ Data obtained at 298 p.s.i.a. instead of 300 p.s.i.a.

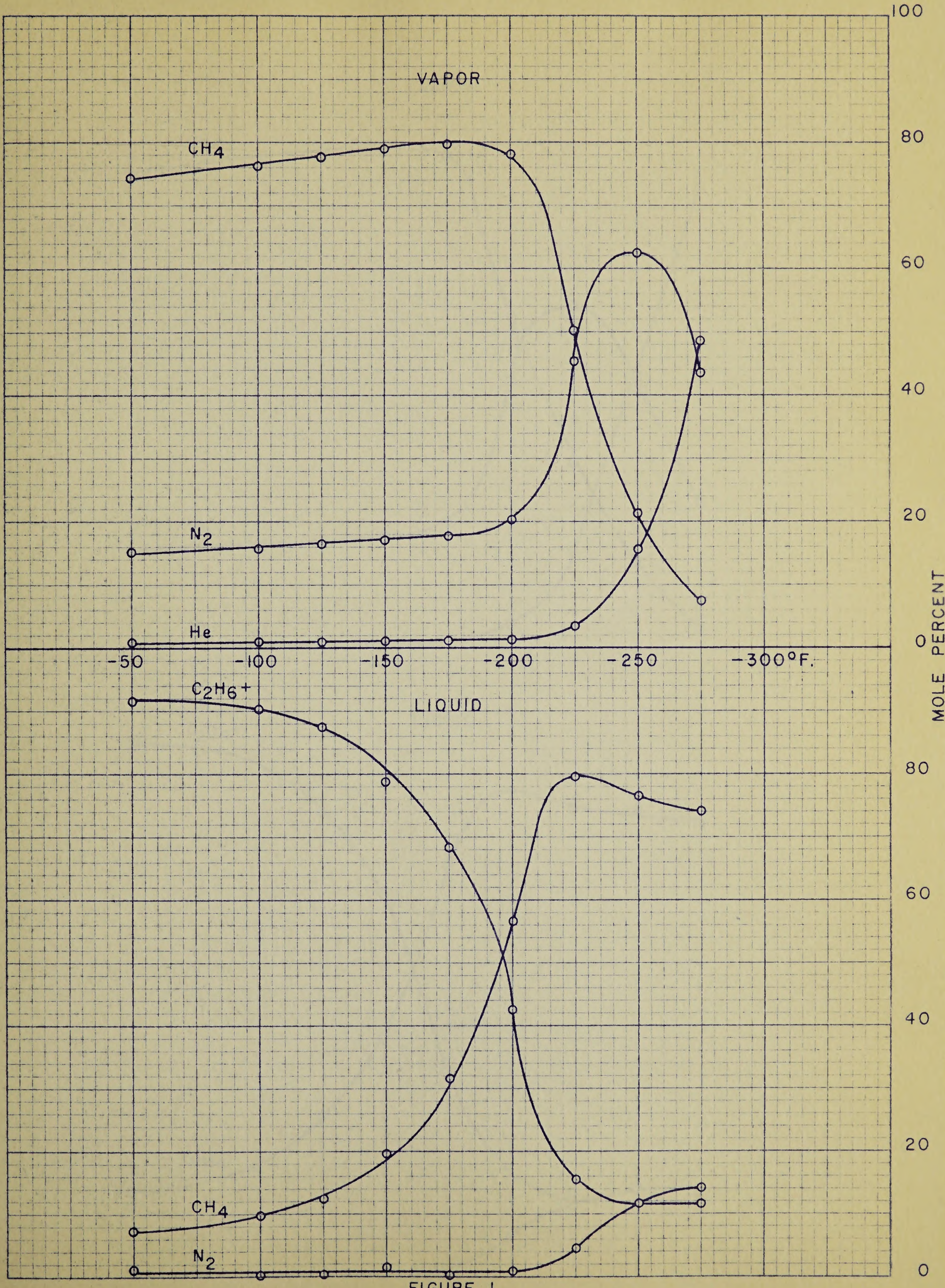

FIGURE 1.
EQUILIBRIUM PHASE RELATIONSHIPS OF EXELL GAS, 100 p.s.i.a.

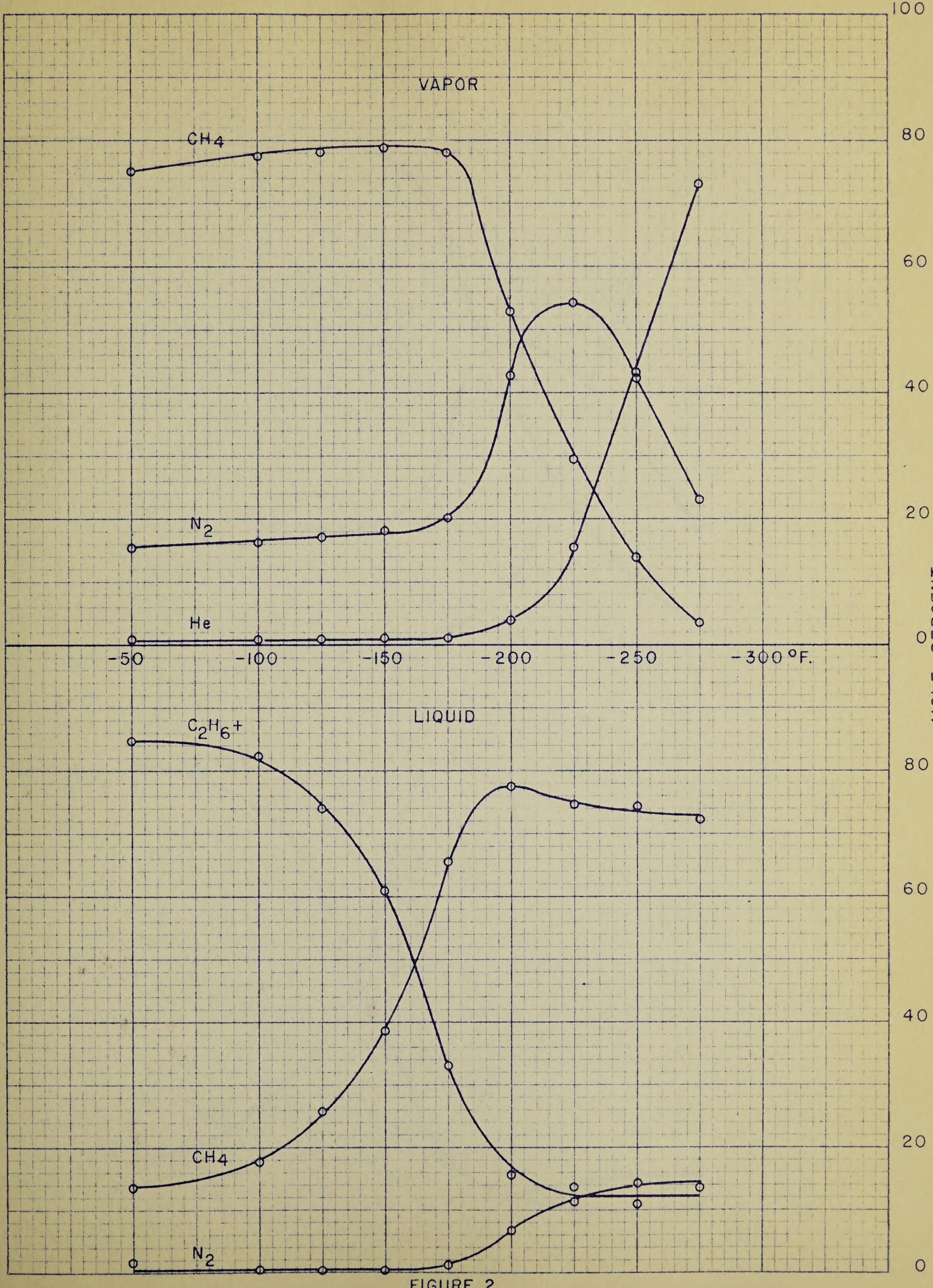

FIGURE 2.
EQUILIBRIUM PHASE RELATIONSHIPS OF EXELL GAS, 200 p.s.i.a.

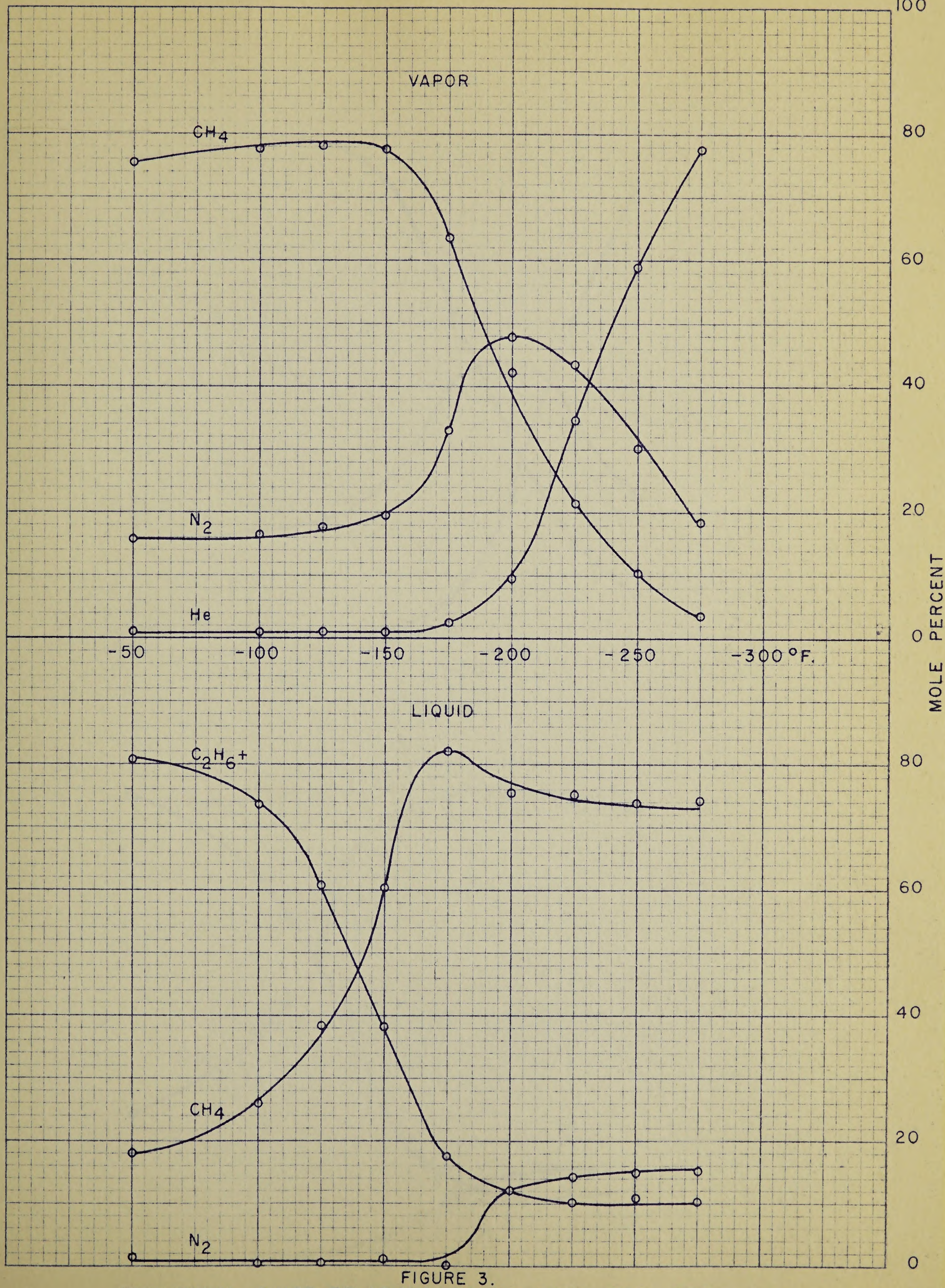

FIGURE 3.
EQUILIBRIUM PHASE RELATIONSHIPS OF EXELL GAS, 300 p.s.i.a.

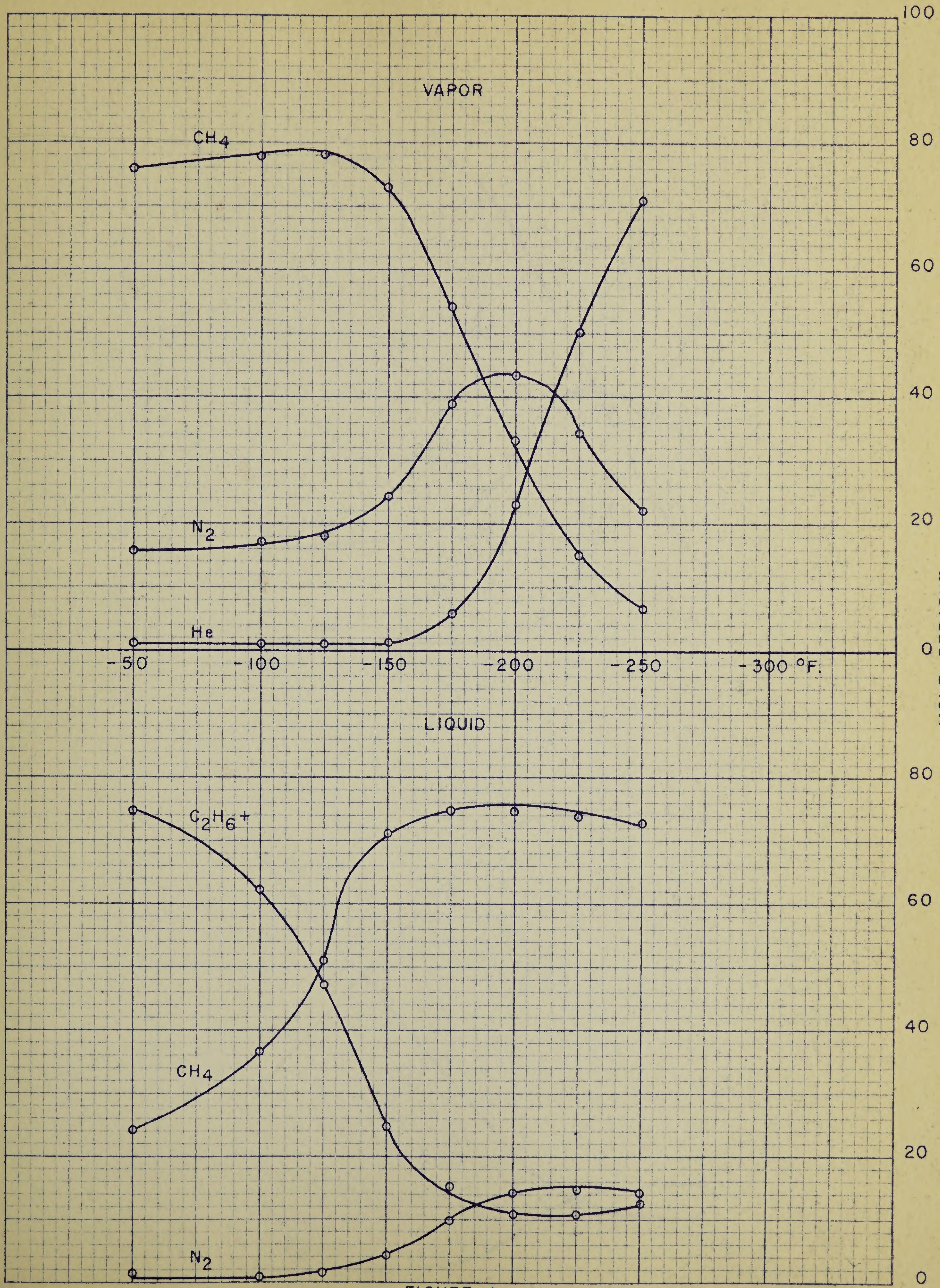

FIGURE 4.
EQUILIBRIUM PHASE RELATIONSHIPS OF EXELL GAS, 400 p.s.i.a.

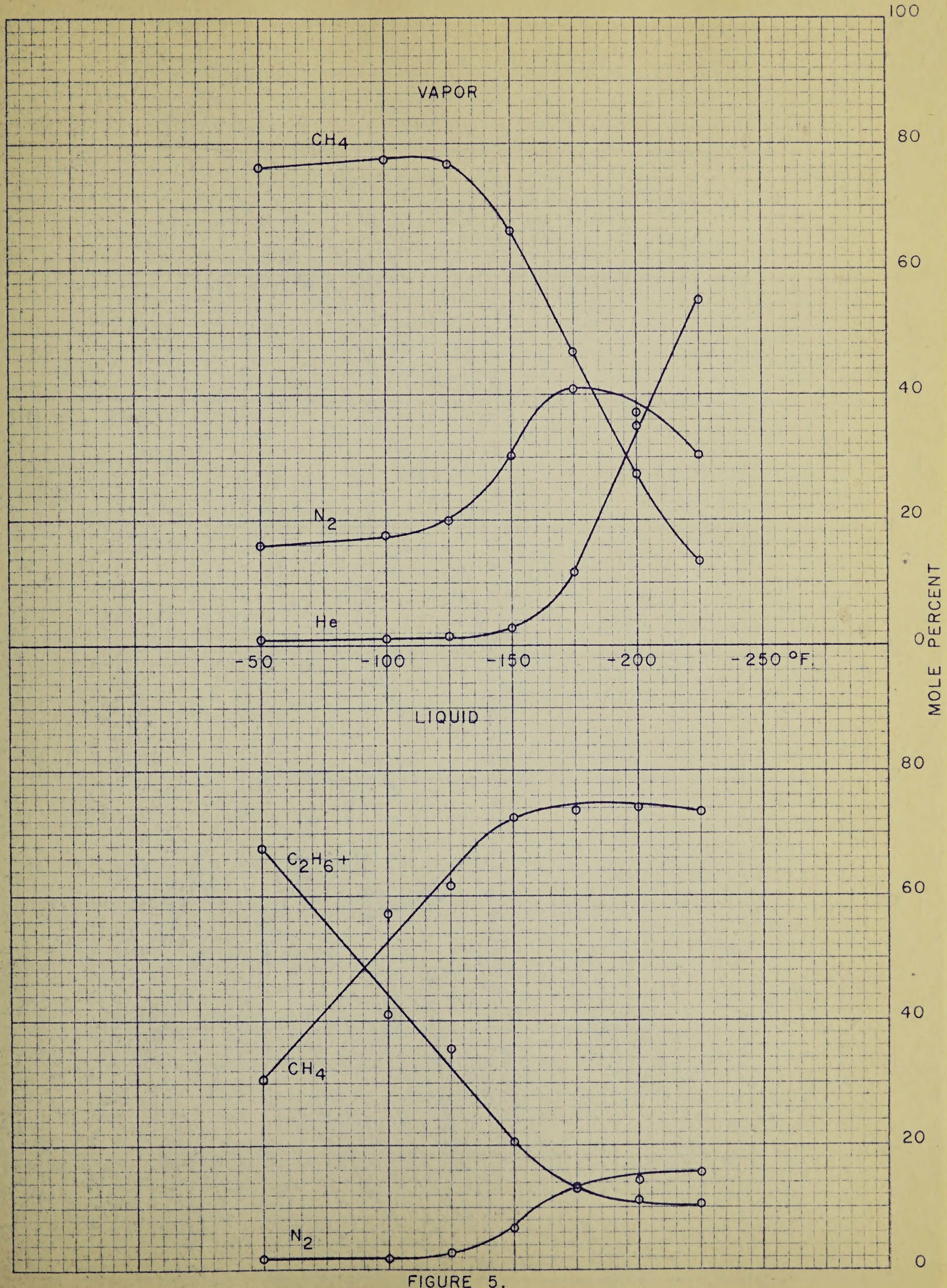

FIGURE 5.
EQUILIBRIUM PHASE RELATIONSHIPS OF EXELL GAS, 500 p.s.i.a.

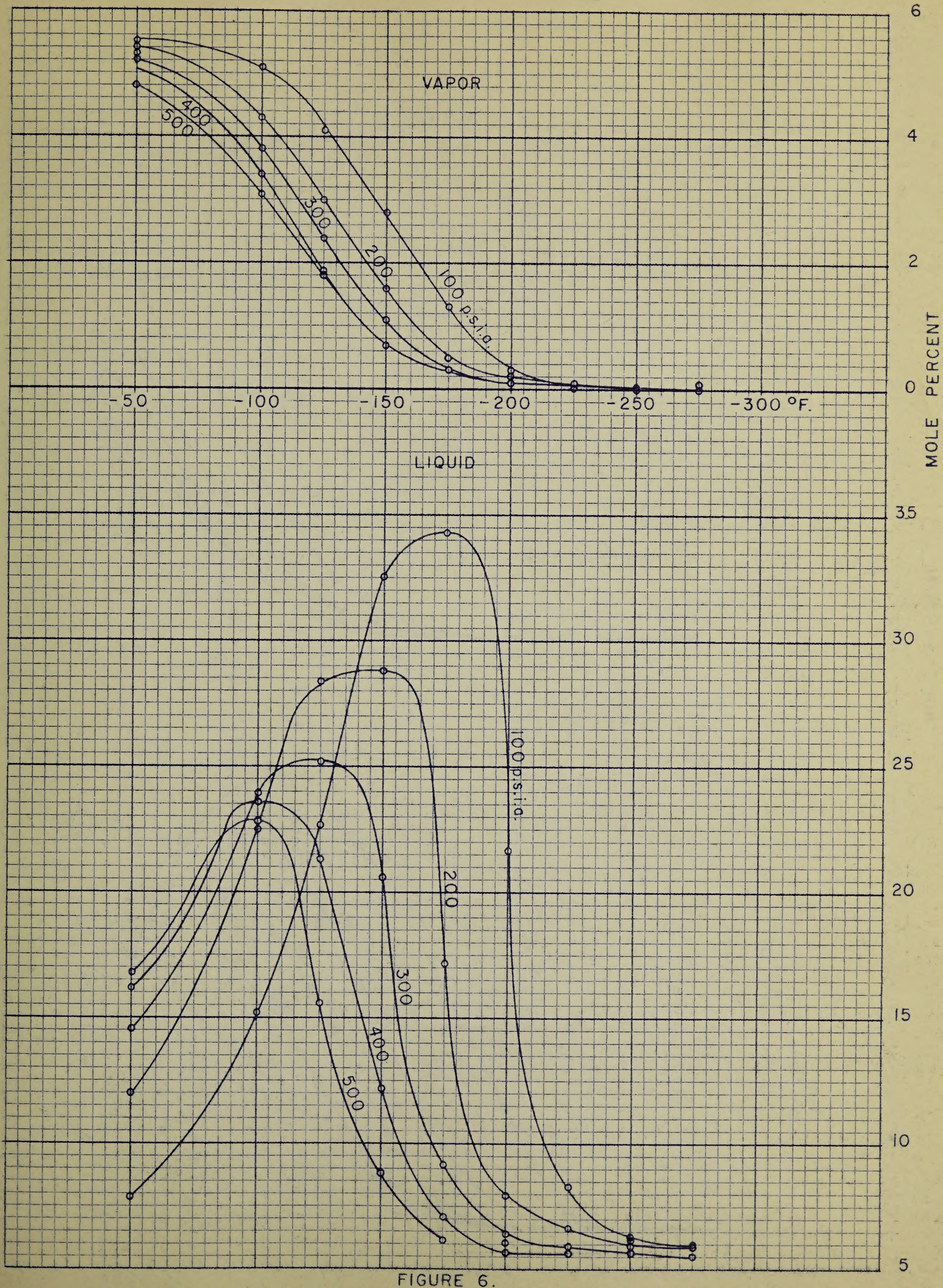

FIGURE 6.
EQUILIBRIUM PHASE RELATIONSHIPS OF ETHANE IN EXELL GAS.

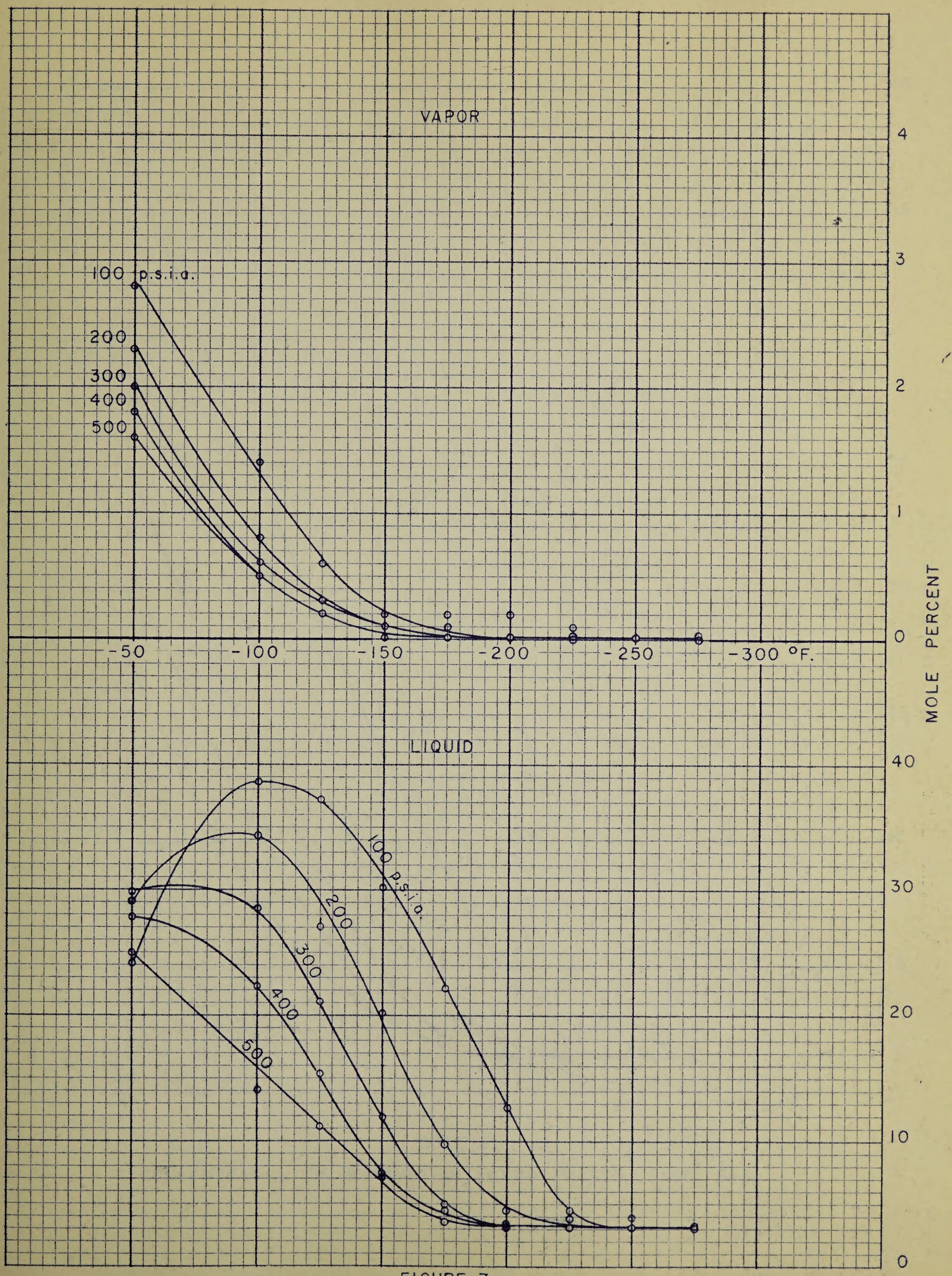

FIGURE 7.
EQUILIBRIUM PHASE RELATIONSHIPS OF PROPANE IN EXELL GAS.

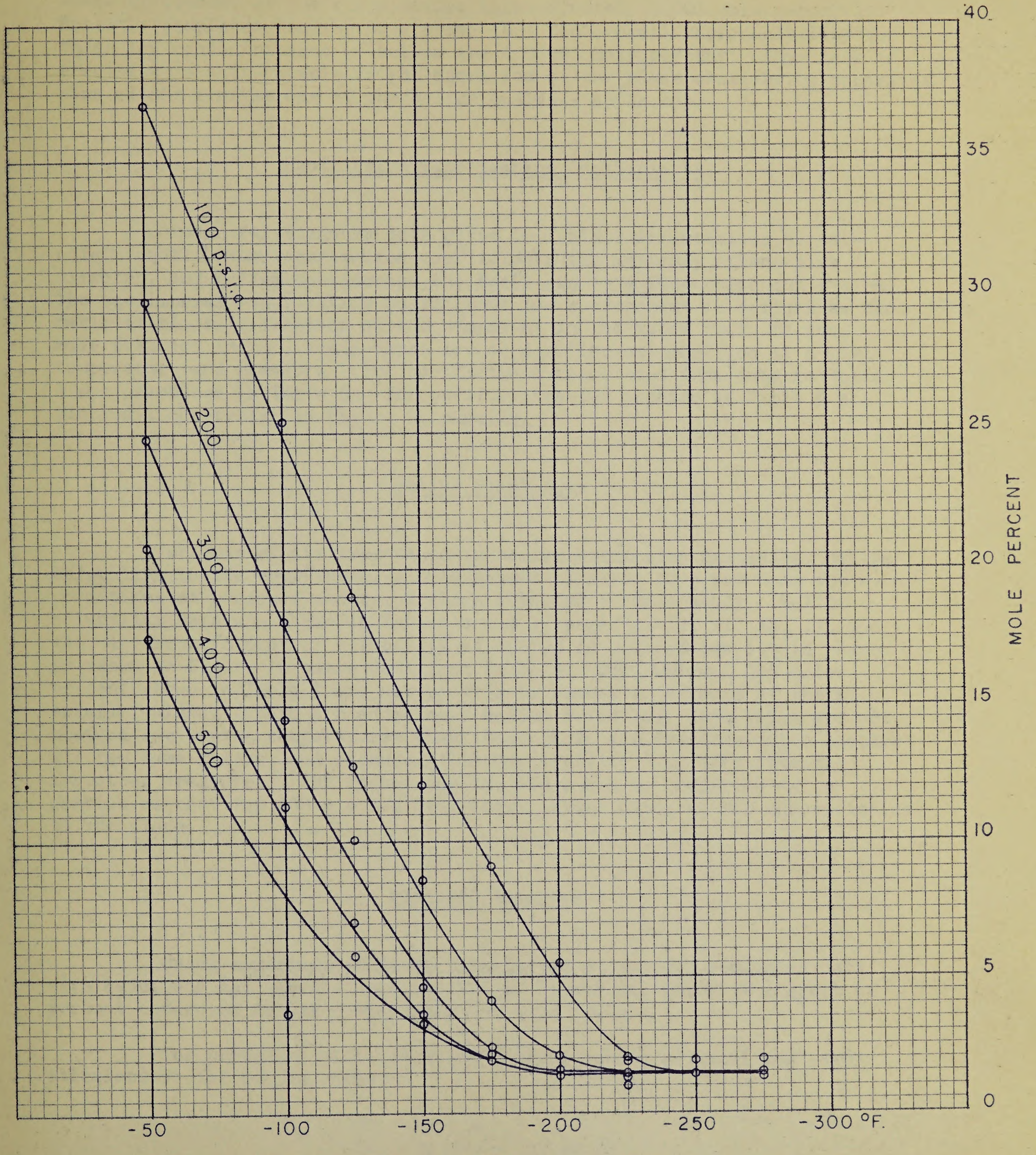

FIGURE 8.

CONCENTRATION OF BUTANES IN LIQUID PHASES, EXELL GAS.

somewhat because of their low values (approximately 0.002 mole percent). Recently completed studies have shown that the overall reproducibility for these low concentrations of helium are ± 0.003 mole percent. This lack of precision is attributable to the operation of the phase equilibrium apparatus plus slight limitations of the helium analysis apparatus.

Equilibrium Vaporization Coefficients

Phase relationship data given in Table 3 are utilized to calculate equilibrium vaporization coefficients for methane, ethane-plus, nitrogen, and helium considering the Exell gas as a four-component system. The equilibrium vaporization coefficient for a component is defined as the ratio of the mole fraction of the component in the vapor phase to its mole fraction in the liquid phase for an equilibrium condition at a given temperature and pressure. The coefficients calculated from data in Table 3 are presented in Table 6. The coefficients for methane in Table 6 are plotted isobarically in Figure 9, page 28.

Helium Solubility

Because of its importance in helium extraction processes, helium solubility in the equilibrium liquid phases is noted in particular for conditions of pressure and temperature obtained in this study. Helium solubility data are shown in Tables 2 and 3, pages 9, 10, 11, 12, 13, and 14. An isobaric plot of solubility of helium in equilibrium liquid phases is shown in Figure 10 using data from Table 3. Data below 0.005 mole percent shown in Table 3 are not plotted in Figure 10 because of their erratic values. There are additional helium solubility data which are not plotted for warmer temperatures than those shown for the respective isobars for the same reason, and because of incompatability with data obtained for other pressures. The isobar for the 100 p.s.i.a. condition and a portion of that for 300 p.s.i.a. are shown dashed owing to the uncertainties in the slope.

Percent Condensed

Using experimental data, calculation of percent condensed data were made, and the results were plotted in Figure 11, which is a graph of percent condensed versus temperature for five isobars.

The procedure utilized essentially a series of trial and error calculations for the equation,

$$\sum_{1}^{j} x_i = \sum_{1}^{j} \frac{n_i}{L+K_iV} = 100.00$$

TABLE 6. - Equilibrium vaporization coefficients of Exell Gas as a four-component system

		Pressure, p.s.i.a.				
		100	200	300	400	500
Temp., °F.	Component	Coefficients				
-50	Methane	10.1	5.410	4.182	3.149	2.485
	Ethane-plus	.103	.0980	.0942	.0977	.0993
	Nitrogen	13.8	11.1	11.3	12.2	8.89
	Helium	900	500	110	220	140
-100	Methane	7.88	4.398	2.981	2.123	1.357
	Ethane-plus	.0743	.0631	.0612	.0624	.0876
	Nitrogen	79	1/	42	19	10.4
	Helium	1000	330	140	140	85.7
-125	Methane	6.167	3.027	2.034	1.534	1.245
	Ethane-plus	.0538	.0445	.0426	.0444	.0562
	Nitrogen	170	1/	45	12.2	7.14
	Helium	330	1100	110	170	63.6
-150	Methane	3.970	2.033	1.292	1.025	.9117
	Ethane-plus	.0381	.0279	.0286	.0405	.044
	Nitrogen	12.1	180	16.4	5.83	4.38
	Helium	370	280	260	114	48.3
-175	Methane	2.533	1.189	.7752	.7282	.6350
	Ethane-plus	.0204	.015	.017	.026	.047
	Nitrogen	180	15.5	330	3.920	3.068
	Helium	180	300	470	85.7	58.62
-200	Methane	1.377	.6843	.5608	.4464	.3698
	Ethane-plus	.0071	.019	.016	.028	.036
	Nitrogen	23	6.37	3.967	3.042	2.576
	Helium	650	235	104	118.7	100.0
-225	Methane	.6308	.3976	.2855	.2070	.1837
	Ethane-plus	.0065	.0072	.0097	.0092	.066
	Nitrogen	9.93	4.789	3.042	2.315	1.961
	Helium	630	541	300.0	210.5	158.0
-250	Methane	.2788	.1882	.1432	.0933	
	Ethane-plus	.0085	.018	.0091	1/	
	Nitrogen	5.269	2.951	2.034	1.552	
	Helium	2300	619	513.0	371.7	
-275	Methane	.0999	.0510	2/ .0512		
	Ethane-plus	1/	.0074	1,2/		
	Nitrogen	3.106	1.655	2/ 1.217		
	Helium	2220	1360	2/ 769.3		

1/ Indeterminate from analyses.

2/ Determined from data obtained at 298 p.s.i.a. instead of 300 p.s.i.a.

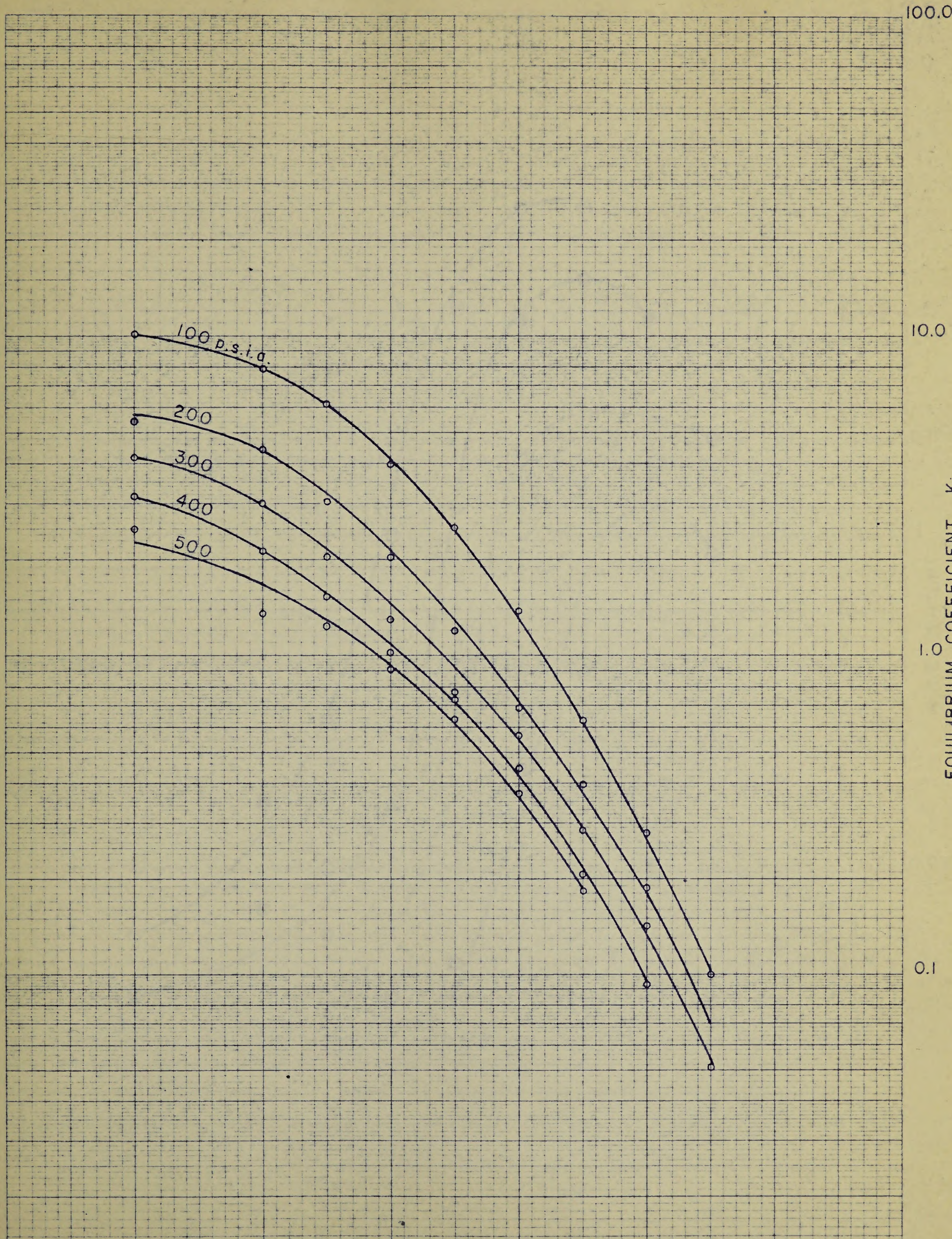

FIGURE 9.– EQUILIBRIUM COEFFICIENTS FOR METHANE, EXELL GAS.

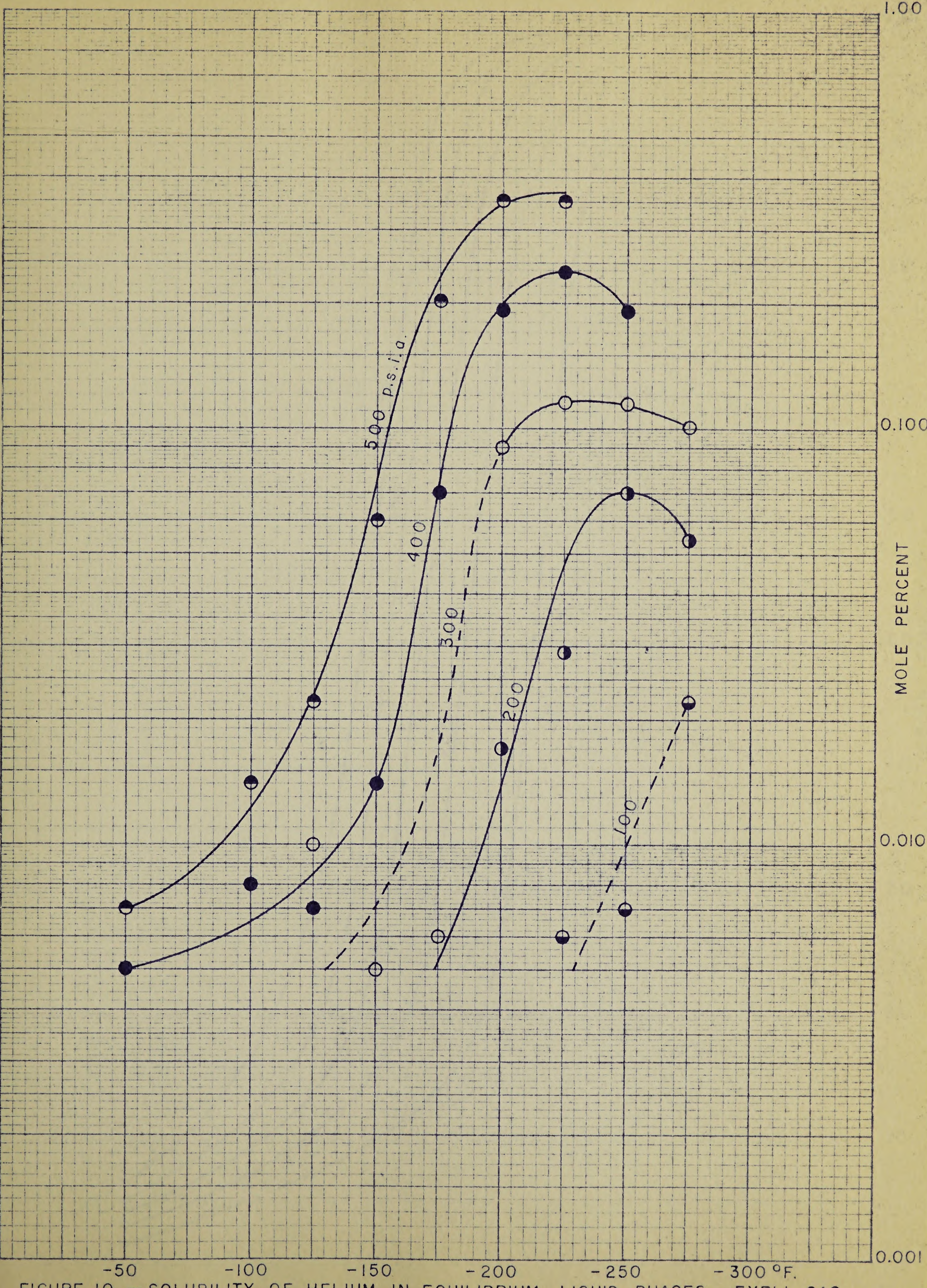

FIGURE 10. — SOLUBILITY OF HELIUM IN EQUILIBRIUM LIQUID PHASES, EXELL GAS.

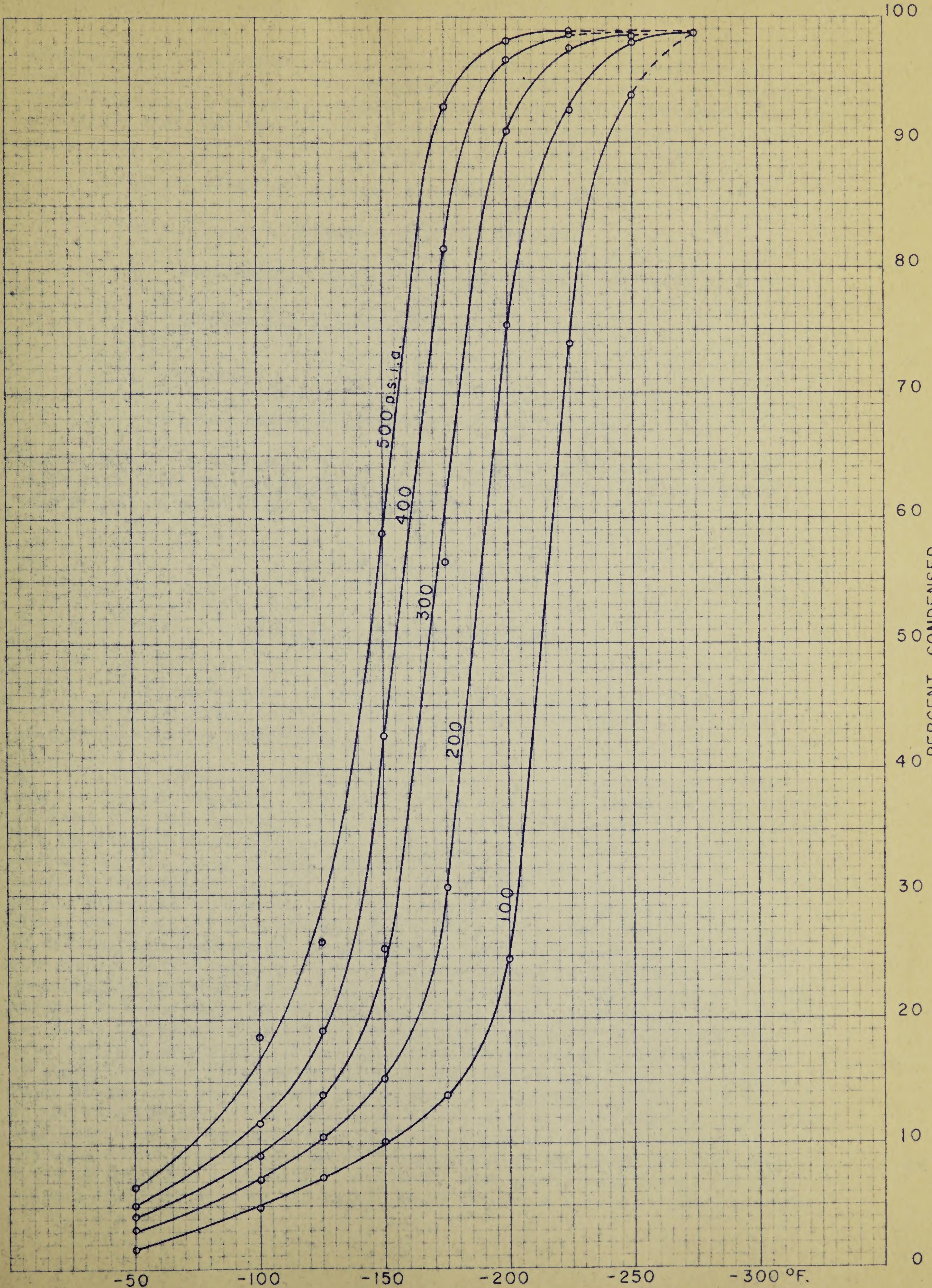

FIGURE 11.– ISOBARIC PERCENT CONDENSED DATA, EXELL GAS.

until a final calculation was made which satisfied this equation within certain tolerance limits. This procedure was used for each of 39 conditions of temperature and pressure included in this phase study. For these calculations, Exell Gas was considered as a four-component system as noted on pages 2 and 6. The terms of this equation are defined as follows:

x_i = percent of component i in the liquid phase

n_i = percent of component i in the feed gas

K_i = experimental equilibrium vaporization coefficient of i

$L = \frac{\text{assumed percent condensed}}{100}$

V = 1.0000 - L

j = total number of components in the feed gas

Values of L are substituted in the equation by trial and error until the value of L is found that gives 100.00 for the summation. A discussion of this method is given by M. B. Standing (6).

DISCUSSION OF RESULTS

Vapor-Liquid Phase Compositions

The compositions of the vapor and liquid phases may be best evaluated by reference to the graphical representation which is a plot of mole percent versus temperature.

The graphs for the Exell gas treated as a four-component system exhibit typical behavior. Reference to the reports for Keyes Gas (4), Cliffside Gas (7), and Typical Helium Conservation Gas (8) reveal the similarities. The equilibrium phase relationships for Exell gas are shown in Figures 1 through 5. The range of temperatures covered is from -50 to -275° F. For selected temperatures in the range of -50 to -225° F., data were obtained at all pressures covered in the study. No data were obtained at either 400 or 500 p.s.i.a. for -275° F., or at 500 p.s.i.a. for -250° F. because of difficulties encountered in sampling at these conditions of high percent condensed. In the vapor phase, the methane content is high at the warm end, and, as the temperature becomes colder, reaches a maximum and drops off sharply to a low value at the cold end of the temperature range. The nitrogen is low at the warm end, reaches a maximum of about 40-60 percent near the cold end, and decreases as the temperature becomes colder. Helium remains at about 1 percent from -50 to -150° F. and then sharply rises to a high value at the cold end. In the liquid phase, ethane-plus content is high at the warm end, drops off sharply to a low value at near -200° F., continuing near this value to the cold end. Methane progresses from a low value at the warm end to a high value in the colder half of the range and falls off slightly from this value at the cold end. Nitrogen is very low at the warm end and continued thus to mid-range, where it starts a gradual rise, reaching

a maximum of low percent near the cold end of the temperature range. The configuration of the curves in both phases are similar with respect to pressure for the five isobars; the effect of pressure shifts the curves along the temperature scale.

In addition to the usual phase relationships noted above, the vapor-liquid data for ethane are shown in Figure 6, page 23, those for propane are described in Figure 7, page 24, and the concentration of butanes in the liquid phase are shown in Figure 8, page 25.

With respect to ethane, some generalizations may be noted. In the vapor phase, a low concentration (about 5%) is present at the warm end which drops off to a very low value (less than 1%) near mid-range; the higher the pressure, the warmer is the temperature at which this lower concentration is reached. In the liquid phase, the concentration rises from a low value to a maximum from which it falls to a low value as the cold end is reached. This maximum is attained near mid-range for 100 p.s.i.a., and as pressures are increased, the maximum appears nearer the warm end and of lower value.

With respect to propane, the following observations are made. In the vapor phase, the concentration drops from a low value at the warm end to a very low value near -175° F.; the higher the pressure, the warmer is the temperature at which the lowest concentrations are reached. In the liquid phase, propane has a moderate value at -50° F., and for the 100 and 200 p.s.i.a. conditions, rises to a maximum before falling off to a low value at the cold end; for the 300, 400, and 500 p.s.i.a. conditions, from a moderate value at the warm end, the concentration falls to a low value near mid-range. Again, as was noted in the instance of ethane, the maximum appears nearer the warm end and of lower value as the pressure is increased. The maximum is not obvious for the 500 p.s.i.a. condition, however.

In Figure 8, page 25, the concentration of butanes in liquid phases are shown to decrease from moderate values at -50° F. to low values at the cold end. The value at -50° F. becomes smaller as the pressure increases.

Equilibrium Vaporization Coefficients

The quotient obtained by dividing the mole fraction of a given component in the vapor phase by its mole fraction in the liquid phase for an equilibrium condition at a given temperature and pressure is known as the equilibrium vaporization coefficient. The designations equilibrium vaporization coefficient and equilibrium coefficient are used interchangeably in this report. The coefficients for components in a system are of importance in engineering design. Because methane and, in many cases, nitrogen are major components of natural gases from which helium is extracted, their equilibrium coefficients assume particular significance in the engineering of helium separation processes. Table 6, page 27, presents coefficients for Exell Gas treated as a four-component system as noted on

pages 2 and 6. At several conditions of temperature and pressure, some of these coefficients appear erratic, particularly for helium, when plotting of results is attempted. Reproducibility tests mentioned previously for helium point to lack of precision as contributing heavily to its apparent erratic behavior.

Equilibrium coefficients for methane are plotted isobarically in Figure 9. Typical behavior is exhibited; the general shape of the curves is similar to that shown for methane in previous studies (4, 7, 8). The coefficients become smaller with decreasing temperatures and, for a given temperature, decrease as pressures are increased for the temperature range studied.

Helium Solubility

The solubility of helium in the liquid phases assumes great importance in the efficiency of helium extraction processes. Helium is usually present in small concentrations (1.0 mole percent in the case of the Exell Helium Plant) in the gas from which plants extract helium; therefore, small amounts appearing in liquid phases are more significant than they might appear otherwise. The extraction process aims to reduce these amounts to promote efficiency consistent with economy.

The helium content in the liquid phases is indicated in Table 3, pages 13 and 14, and Figure 10, page 29.

Figure 10 shows the effect of temperature and pressure on the solubility of helium in the equilibrium liquid phases. For the temperature ranges covered by the respective isobars that are shown, the solubility increases from a low value as the temperature becomes colder until a maximum is reached for each curve for the 200, 300, 400, and 500 p.s.i.a. conditions. An increase in solubility as the temperature decreases is also noted for the 100 p.s.i.a. condition.

Percent Condensed

Figure 11, page 30, presents plots of percent condensed versus temperature for each of five pressures. The curves exhibit typical behavior; for any given temperature within the range studied, the percent condensed increases as the pressure increases. Dashed lines which are extended beyond points plotted at the cold end for several isobars indicate the expected trned if temperatures had been reduced to -275° F.

BIBLIOGRAPHY

1. BRANDT, L. W. AND STROUD, L., An Experimental and Theoretical Study of the Phase Relationships of Navajo Gas, Bureau of Mines, Helium Division, Region VI, Research Branch, Internal Report No. 4, April 5, 1954, 45 pp.

2. BRANDT, L. W. AND STROUD, L., A Windowed Equilibrium Cell and Phase Equilibrium Apparatus for Pressures to 800 P.S.I.G., Bureau of Mines, Helium Activity, Division of Research, Internal Report No. 10, December 27, 1955, 33 pp.

3. BRANDT, L. W. AND DEATON, W. M., Thyratron-Controlled Stirrer or Pump for Pressurized Systems, Rev. Sci. Instr., vol. 27, No. 9, September 1956, pp. 714-715.

4. BRANDT, L. W., STROUD, L., AND BRUCE, H. E., An Experimental Study of the Phase Relationships, Dewpoints, and Compressibility Factors of Keyes Gas, Bureau of Mines, Helium Activity, Division of Research, Internal Report No. 14, October 1, 1956, 30 pp.

5. FROST, E. M., JR., Improved Apparatus and Procedure for Determination of Helium in Natural Gas, Bureau of Mines, Rept. of Investigations 3899, 1946, 16 pp.

6. STANDING, M. B., Volumetric and Phase Behavior of Oil Field Hydrocarbon Systems, Reinhold Pub. Corp., N. Y., N. Y., 1952, pp. 50-51.

7. STROUD, L., MILLER, J. E., AND SEITZ, C. A., An Experimental Study of the Phase Relationships of Cliffside Gas, Bureau of Mines, Helium Activity, Division of Research, Internal Report No. 19, May 25, 1959, 28 pp.

8. STROUD, L., MILLER, J. E., AND BRANDT, L. W., An Experimental Study of the Phase Relationships of a Typical Helium Conservation Gas, Bureau of Mines, Helium Activity, Division of Research, Internal Report No. 20, July 24, 1959, 36 pp.

9. STROUD, L., MILLER, J. E., AND BRANDT, L. W., Supplement to Open File of Information and Data Relating to the Extraction of Helium from Natural Gas by Low-Temperature Processes, Bureau of Mines, Helium Activity, August 6, 1959, 36 pp.